N64 - 19794

NASA CR-53898

Technical Report No. 32-567

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in the Gas Phase and in Liquid Nitrogen,

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February, 1964

Hartley Band Extinction Coefficients of Ozone in the Gas Phase and in Liquid Nitrogen, Carbon Monoxide, and Argon

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In the course of work on the photolysis of O_3, we have determined the O_3 extinction coefficients in the region 2000–3100 Å. in liquid N_2 and CO at 77.4°K. and in liquid Ar at 87.5°K. Previously, O_3 extinction coefficients have been reported in aqueous solvents[1-4] and in CCl_4,[5] but the only data for low temperature solvents are those of Kirshenbaum and Streng[6] for the visible absorption of O_3 in liquid O_2.

In the gas phase, differing extinction coefficients in the Hartley band were reported by Ny and Choong,[7]

(1)   H. Taube, *Trans. Faraday Soc.*, **53**, 656 (1957).

(2)   J. Weiss, *ibid*, **31**, 668 (1935).

(3)   M. G. Alder and O. R. Hill, *J. Am. Chem. Soc.*, **72**, 1884 (1950).

(4)   M. L. Kilpatrick, C. C. Herrick, and M. Kilpatrick, *ibid*, **78**, 1784 (1956).

(5)   G. W. Robinson, M.S. Thesis, Georgia Institute of Technology, 1949.

(6)   A. O. Kirshenbaum and A. G. Streng, *J. Chem. Phys.*, **35**, 1440 (1961)

(7)   T.-Z. Ny and S.-P. Choong, *Chinese J. Phys.*, **1**, 38 (1933).

Vigroux,[8] and Inn and Tanaka.[9] The Inn and Tanaka results have subsequently been verified closely by Hearn[9] at six wave lengths and are considered to be the most reliable values available. We have measured the gas phase extinction coefficients throughout the region 2000–3100 Å. and our results are in close agreement with those of Inn and Tanaka.

Experimental

Reagents. Ozone was prepared by a Tesla coil discharge in purified O_2 and stored at $77°K$. Transfer of O_3 to the absorption cells was accomplished by distillation from a liquid argon bath and collection at $77°K$. Following the transfer, residual traces of O_2 were removed by pumping on the O_3 under high vacuum.

The solvents (N_2, Linde high purity dry; CO, Matheson C.P.; Ar, Linde tank grade) were passed through a Drierite–Ascarite column, liquefied, and further purified by two distillations, taking the center fraction in each case. Argon was handled using liquid argon as a coolant.

Apparatus. Spectra were recorded on a Cary Model 11 spectrophotometer. The wave length scale was calibrated by means of a low pressure mercury arc, and the wave lengths reported in this work are considered reliable to ± 2 Å.

Gas phase spectra were taken in a 5-cm. cylindrical quartz cell, the O_3 being sealed off in the cell under vacuum.

The liquid cell was a 1-cm. cylindrical quartz cell, with an annular quartz jacket for the coolant, suspended in a vacuum canister with quartz windows. The entire unit could be placed in the spectrophotometer. Since the light path did not pass through the coolant and the solution was free of turbulence, the quality of the spectra was comparable to that of ordinary room temperature solvents. Optical densities of aqueous solutions of chromium nitrate were found to be identical within 0.5% in the above cell and in standard 1-cm. cylindrical cells, with an appropriate zero correction.

Measurement of gaseous O_2, from decomposed O_3, was done by means of a calibrated gas buret which was similar in construction to a McLeod gage, with the exception that the measuring stem had a stopcock to permit the O_2 to be collected by Toepler pump action. Calibration of the gas buret was checked by measurement of known samples in a standard volume at a pressure measured on a 0–20 mm. Wallace and Tiernan gage which was calibrated by means of a McLeod gage. The gas buret is considered accurate to 2% or better.

Methods. Ozone concentrations in the low temperature solvents were determined by separately measuring the amount of O_3 spectrophotometrically in gas cells, using the relation

$$[O_3]_{\text{solvent}} = [O_3]_{\text{gas}} V_{\text{gas}} / V_{\text{solvent}}$$

The volumes, V_{gas} and V_{solvent}, were determined by filling the cells with water from a buret or by weighing the water. To ensure against errors due to loss of O_3 in transfer, the following three separate methods were employed in the initial experiments with N_2 solvent.

Method 1. The O_3 peak optical density (2553 Å.) was measured in a sealed-off gas cell and the O_3 was then transferred to the liquid cell at $77°K$., using glass blown connections and break-off seals exclusively. In transfers of this type all glassware in contact with the O_3 sample was pre-exposed to O_3 at higher pressures. The solvent was then condensed into the cell and the spectrum was recorded. Zero corrections for the liquid spectra were made by taking the spectrum of the cell containing solvent only.

Method 2. The spectrum was first recorded in solution, followed by removal of the solvent by pumping at $77°K$. and subsequent transfer of the O_3 to the gas cell. Although more difficult than method 1, this technique gave results which were within 1% of those of method 1. Since methods 1 and 2 give upper and lower limits, respectively, for O_3 concentrations in solution, convergence of the results eliminates the possibility of error due to O_3 loss in transfer.

Method 3. In this method, which was the simplest experimentally, gaseous O_3 was placed in the low temperature cell and the spectrum was recorded. The O_3 was then condensed by addition of coolant to the annular jacket and the solvent was condensed into the cell, and the spectrum was then taken. Although this method suffered somewhat from an unfavorable volume ratio (the volume of O_3 in the light path was about $^1/_6$ the total gaseous volume), the results were equal to within 1% of those from methods 1 and 2. Therefore, method 3 was used exclusively for the solvents Ar and CO.

Ozone concentrations in the gas phase were determined by converting the O_3 to O_2, by means of heat or a Tesla spark coil, and then measuring the O_2 in the gas buret. The technique was as follows: a sample of pure O_3 was sealed off in the (well-baked out) 5-cm. cell, with two break-off seals attached, and the peak (2553 Å.) was measured. The cell was immediately placed in liquid N_2 to quench O_3 decomposition, and the

(8) E. Vigroux, *Ann. phys.*, **8**, 709 (1953).

(9) E. C. Y. Inn and T. Tanaka, "Ozone Chemistry and Technology," Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D. C., 1959, p. 263; *J. Opt. Soc. Am.*, **43**, 870 (1953).

cell was then opened to high vacuum by means of one of the break-off seals. After removal of any O_2 or other volatile gases, the cell was resealed (while pumping) and the O_3 was decomposed. The cell was then placed in a Dry Ice bath and attached to the gas buret, and the O_2 was admitted to the gas buret through the second break-off seal.

Table I: Ozone Extinction Coefficients Obtained by Different Workers (cm. NTP)$^{-1}$

| Wave ength, Å.	Inn and Tanaka	Present work	Hearn
2102	6.39	6.33	
2152	11.7	12.1	
2202	21.0	21.4	
2252	34.3	34.8	
2302	52.8	53.5	
2352	73.6	74.6	
2362	78.2	79.8	
2372	83.2	84.1	
2382	86.2	88.9	
2392	90.1	93.1	
2402	95.3	97.3	
2412	98.9	102	
2422	103	105.5	
2432	107	110	
2452	116	118	
2478	124	125	
2500	130	130	
2519	133	134.5	
2537	(133.1)[a]	135	133.9
2539	134	135	
2553	135	137	
2587	133	134.5	
2604	128	129	
2624	123	123.5	
2643	118	117.5	
2675	103	103	
2702	89.1	91.1	
2752	66.6	66.9	
2802	43.6	45.6	
2852	27.5	28.0	
2894	(17.1)[a]	17.3	17.2
2902	15.5	15.6	
2952	8.33	8.5	
2967	(6.72)[a]	6.85	6.97

[a] As interpolated by Hearn, ref. 9.
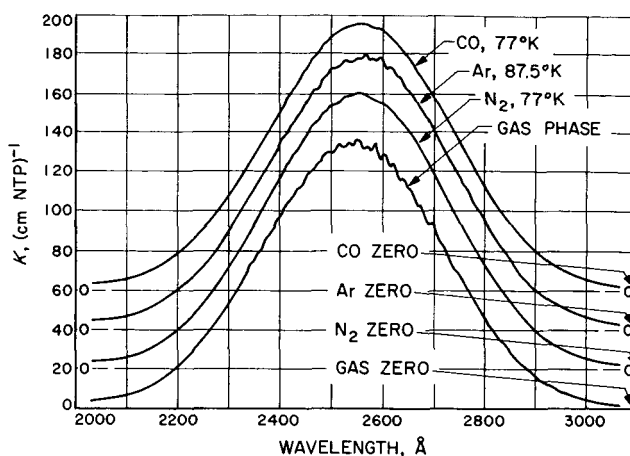
Figure 1. Extinction coefficients of zone. (To obtain K values for N_2, Ar, or CO, subtract 20, 40, or 60, respectively, from the value indicated on the ordinate.)

Extinction coefficients at other wave lengths in the region 2000–3100 Å. were then determined relative to the peak value by taking the spectrum of O_3 with about 10 cm. added O_2 (no pressure effect was noted). This method has the advantage that O_3 decomposition is sufficiently inhibited so that no corrections are necessary.

Results and Discussion

The extinction coefficients of O_3 in liquid N_2, CO, and Ar, and in the gas phase, are shown in Fig. 1. The concentration ratios were determined to within 2% and therefore, coupled with a 2% uncertainty in the gas phase extinction coefficients, the solvent values are believed to be reliable to within 4%.

Values for the gas phase extinction coefficients obtained by Inn and Tanaka, Hearn, and in the present study are listed at several wave lengths in Table I. Our results are for the most part 1 or 2% higher than the Inn and Tanaka values, and near the maximum seem to be in better agreement with the values found by Hearn. Agreement with the Inn and Tanaka results is poorest in the region from about 2375 to 2450 Å., where the Inn and Tanaka values fall as much as 3% below ours. We have rechecked out data in this region and find no error.